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A request for examination according to § 44 Patent Law has been established

Granular washing- and cleaning agents of higher bulk density, free of dust and fine particles

The invention relates to new multi-component washing- and cleaning agents pourable and free-flowing, with higher density and simultaneous good solubility in cold water. The new agents are developed to be abrasion resistant goods, free of dust and fine particles, of the following particle structure: a compacted core having good adhesion formed of one or more valued materials and/or auxiliaries, which are soluble in aqueous float and/or are finely dispersed insolubles, is encapsulated by a mixture of similar and/or further valued materials and/or auxiliaries with - in relation to the diameter of the core material - smaller individual particle sizes. For this purpose, the particles of the encapsulating substances are incorporated into a binder which is solid at room temperature and is soluble in cold water, and are combined on the outer surface of the core material.

In a further implementation, the invention relates to the process of manufacturing the new form on offer of such washing- and cleaning agents.

**The following data have been extracted from the documentation filed by the Patentee**

**Description**

The invention relates to a new form on offer of a multi-component washing-, and cleaning agent pourable and free-flowing, particularly a textile detergent which combines high density and also good solubility in cold water, and is free of dust- and fine particles, and thus facilitates a greater freedom of choice of valued- materials and auxiliaries to be inserted into the multi-component mixture.

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The increasing raising of bulk densities of conventional detergent granulates on the market, is mainly achieved by a compact core structure of the granulates always being used, which however is connected - as a negative accompanying phenomenon - with an increasing retardation of solubility. This undesirable retardation of solubility is thereby solved, among other things, by a series of anionic and non-ionic surfactants, common in practice, and above all by corresponding surfactant mixtures, which on dissolving in water have a tendency to form gel phases. Already with surfactant contents of 10% by weight and over, in relation to the multi-component mixture, it can lead to undesirable and solubility retarding gelling, when dissolving in particularly cold water.

EP-B-0 486 592 describes granular or extruded washing- or cleaning agents with bulk densities above 600 g/l, which contain anionic and/or non-ionic surfactants in quantities of at least 15% by weight, and up to about 35% by weight. They are manufactured by a process, in which a solid free-flowing pre-mix, containing a plasticiser and/or lubricant, is compressed into strands at high pressures between 25 and 200 bar, and after emerging from the moulding hole, the strands are cut into the predetermined granulate dimension by means of a cutting device. The manufactured extrudates can subsequently be mixed with other granulates, whereby in an advantageous implementation, the portion of extrudates in the finished washing- or cleaning agents, amounts to more than 60% by weight.

It is known from the International Patent application WO-A-93/15180, that the speed of dissolving of extruded agents can be improved, if short-chain alkyl sulphates are inserted in the pre-mix, particularly C<sub>8-15</sub>-alkyl sulphates, which can be introduced into the pre-mix by specified ways and means. These measures are however not sufficient in all cases, to increase the speeds of dissolving of the complete agent.

The older German Patent application of the Patentee according to DE 195 19 139 (H 1795) proposed to solve the conflict between a high degree of compression of the valued material mixture, particularly by extrusion, regarding on the one hand, the simultaneously required swift solubility of the valued goods already in the early phase of a washing process, particularly free of gelation, and to design granular washing- or cleaning agents with a bulk density over 600 g/l, containing an extruded component as well as anionic and/or non-ionic surfactants in quantities of at least 15% by weight, in such a way, that at least two different granular components are provided for insertion into the multi-material mixture, of which at least one is extruded and at least one is not extruded. The extruded component(s) should thus be contained in quantities of 30 to 85% by weight, in relation to the total agent, whereby simultaneously, the quantities of surfactants (inclusive of soaps) in the extruded component(s), amount to 0 to less than 15% by weight, in relation to the corresponding extruded component. Present in a multi-component mixture is at least one non-extruded granulate, and a component containing surfactants, in such quantities that by this, components, at least 1% by weight of surfactants are made ready,

in relation to the total agent, whereby it is further preferred to provide non-extruded granular components containing surfactants in the differently manufactured material mixtures in such quantities, that thereby up to 30% by weight, and preferably 5 to 25% by weight - in relation to the total multi-material mixture of surfactants are made ready. The weight ratio of extruded components containing surfactants to granular components containing non-extruded surfactants, preferably lies in the range of 6 : 1 to 2 : 1, preferably in the range of 5 : 1 to 3 : 1. The subject matter of the disclosure of this older application is thereby expressly also the subject matter of the disclosure of the submitted invention.

If also through such a mixture of differently manufactured multi-components, of which at least one agent is highly compacted by means of extrusion, it leads to an improved compromise between the aimed-at high bulk density of the multi-component mixture, and the simultaneously required sufficiently swift solubility free of gelation, then nevertheless a series of new problems is thereby created. The ideal presentation of uniform particles which correspondingly contain the total components of the multi-material mixtures, must be abandoned. Separation procedures can thereby occur, and corresponding fluctuations in the reproducibility of the aimed-at washing- and cleaning results. The extruded material portion is not only of higher density, and the dried extrudate particles are simultaneously comparatively hard. Under the conditions of transport, storage and insertion, the comparatively softer granulate portion can thereby be exposed to mechanical forces, which can lead partially to its diminution, and thereby to the formation of dust- and fine particles due to friction.

### **The task of the invention**

The conception according to the teaching of the invention is inserted here. The invention has set the task of making available, highly compacted multi-component mixtures in the field of washing- and cleaning agents, and here particularly in the field of textile detergents, which correspond to the old wished for presentation, to be able to unite all components of this known highly complex mixture into one particle. The new particulate goods, in a manner of speaking, should therefore combine the contradictory material properties of high compression and thereby higher bulk density on the one hand, with simultaneous good dispersibility and solubility - ~~particularly also~~ already in the rinsing-in phase using conventional cold mains water in household washing machines.

There is more, over and above the task set in the embodiment of the invention. The new form of supply on offer of the highly compacted textile detergent, should also facilitate a controllable retarding of the solubility of certain parts of the multi-material mixture, and in this manner - particularly with simultaneous incorporation of swiftly soluble components - facilitate a multi-stage washing- and cleaning process, as is the subject matter for example, of the older German Patent application of the Patentee, according to P 44 38 850.0. The disclosure of this older application is thereby also made

the subject matter of the submitted invention disclosure. Described there particularly is a conditioning of the aqueous float and/or the goods to be cleaned in the early phase of the washing process, by incorporation also of complex formers for the multi-valent cations of water hardness, swiftly soluble in cold water, and corresponding mixtures with surfactant compounds soluble in the cold.

The conception of the technical teaching described in what follows, arises particularly from the task, to be able to offer from many points of view, highly sensible material mixtures of textile detergents available nowadays, in a uniform spherical form free of dust- and fine particles, which fulfil all the represented requirements, but simultaneously also however, leaving open the possibility of permitting further modified amendments to the respective recipes of multi-material mixtures, without having to undertake fundamental alterations of the desired form on offer of the multi-material mixture. The teaching in the embodiment of the invention will simultaneously design wide access to the technical realisation of this task in such a way, that on the basis of technology available nowadays to corresponding manufacturers, the technical realisation of the desired presentation is possible without substantial alterations in apparatus.

### **Subject matter of the invention**

The subject matter of the invention is correspondingly in a first implementation, to facilitate a multi-component washing- and cleaning agent capable of being dispensed, and free-flowing, particularly multi-component textile detergents, that combine high density with good solubility also in cold water, and thereby enlarged freedom of selection of valued- and optional auxiliaries. The teaching in the embodiment of the invention is thereby characterised in that these new forms on offer of multi-component mixtures, are formed as abrasion resistant goods, free of dust and fine particles, with the following particle structure:

- each particle contains in its interior, a compacted core having good adhesion, from one or more valued- and/or auxiliary materials, which are soluble in an aqueous float, and/or insoluble in finely dispersed form - in what follows also termed as "core material".
- this core material is encapsulated by a mixture of similar and/or further valued-materials and/or auxiliaries, whose solid material portion possesses an individual particle size, which is less than the diameter of the core material - in what follows also termed as "encapsulating substance".
- thus these particles of the encapsulating substance have incorporated a solid binder also soluble in cold water, and solid at room temperature, and are combined on the outer surface of the core material - and in the description of the invention this binder is also termed "binder".

The teaching in the embodiment of the invention in the preferred implementation, thus provides that with the access of water, the gel-forming and/or only slowly soluble components of the multi-material mixture are the least preponderate part of the constituents of the encapsulating substance, whereby this portion is incorporated into the enveloping substance with correspondingly predetermined individual particle sizes. Its cohesion is guaranteed here by the binder which is solid at room temperature, and the moderately higher temperatures which occur in practice. On access of water, the binder dissolves, already at the temperatures of conventional cold mains water. Isolated in the encapsulating substance by the binder, and separated from each other, slowly soluble and optionally gelled solid particles are present dispersed in the float without coagulation, or being able in any other way to impair the rinsing-in procedure and/or washing process. Through the additional measures described in what follows - for example by the incorporation of dispersing- and/or dissolving auxiliaries - this process of the destruction of the encapsulating substance into fine particles, can be promoted almost optionally.

The nature and particularly solubility of the core material, which is present as a highly compacted article, and usually present in the respective sphere in the form of only a particle - in what follows termed "carrier particle" - is so selected, that preventing the solubility and dispersion of the multi-component mixture, is excluded.

Particularly in the encapsulating substance, almost any optional fine particulate to dusty components can be present and consolidated, which after their release by the primary step of dissolving the binder, can fulfil their assigned task in the scope of the washing- and cleaning processes. It is immediately obvious that as constituents of the encapsulating substance, not only selected individual components are suitable, but particularly optional selected and assembled multi-material compounds can be inserted here, which are separated from neighbouring particles in the form on offer of the preferred spherical dried goods, and thus protected from an undesirable interaction. Such fine particulate multi-material compounds in the encapsulating substance can thus be so co-ordinated on top of each other, that predetermined technical effects during or after dissolving in the wash float can be made to run in optimised form.

The composition of the solid core material - the carrier particle - is likewise variable and selectable within a comparatively wide range, in the scope of the multi-component mixture which is available. The selection of component(s) is governed on the one hand by the requirements of a sufficient solubility in the scope of the washing process - without for example difficulties caused by loosening gel formation - and on the other hand by a superior conception regarding, for example, the pH of the washing float of multi-stage washing and cleaning processes. The carrier particle can consist of a specified selected component, but particularly however also of a correspondingly selected multi-component mixture compacted together. More detailed data in this respect will be found in the following individual items of the teaching in the embodiment of the invention.

In a further implementation, the submitted invention relates to the process of manufacturing the washing- and cleaning agent in the specified spatial arrangement represented here. In the widest interpretation of the process, it is characterised by agglomerating or granulating the core material in the form of a pre-constructed carrier particle with the finely divided goods of the encapsulating substance in the presence of the binder in a form of a preparation capable of free flow, and then consolidating with the binder. The binder, particularly when incorporating a dissolving- and/or emulsifying auxiliary - preferably as an aqueous solution and/or emulsion - can arrive for insertion with simultaneous or subsequent drying, but however it is preferred to insert the binder in the form of a melt, to apply it with the goods to be united, and then by subsequent cooling the coated goods, ensuring the consolidation of the multi-material mixture. The individual items in this respect can be seen in the following description of the invention.

### **Individual items of the teaching in the embodiment of the invention**

Before entering in greater detail into the individual determining elements of handling according to the invention, its conceptual connection is first of all represented as follows: The selection and establishment in concrete individual cases of selected combinations of individual elements will then become accessible in the light of general technical knowledge.

In the core, the invention will restore the spatial arrangement of a multi-component washing- and cleaning agent preparation in the dry condition on the 1-particle. These particulate goods will thus contain all, or practically all the constituents for cases of application. Basically, the principle will be translated into reality, as described for example in the previously cited EP-B-04 86 592. In particular, the teaching in the embodiment of the invention will also facilitate in concrete particulate form, the spherical or cylindrically rounded form on offer of such solid multi-material mixtures.

Deviating from the exact State of the Art in the cited publication, the teaching in the embodiment of the invention will however now provide a separation of the valued- and/or auxiliary materials within each individual sphere in a multiplicity of separated spaces in the dry condition. In this connection, it deals first of all with the inner core, the "core material", and the "encapsulating substance" located as an envelopment of this core. The encapsulating substance - independently of the number of its individual constituents - can be constructed as a single shell, or as several shells. The storage spaces for the multi-material goods to be stored in the dry condition, which result in this manner, can be in immediate contact with each other, but however can also be additionally separated from each other by means of separating layers.

The conception in the embodiment of the invention, furthermore provides for the shell(s) of the encapsulating substance, on their part, to be sub-divided into an optional number of many smaller individual spaces, in which the comparatively fine particulate

valued- and/or auxiliary materials of the encapsulating substance shell(s) are stored contact-free, and nevertheless in a dense packaging. This is achieved by the conception in the embodiment of the invention, by introducing a binder soluble in cold water, as an additional component in the encapsulating substance(s).

The binder component in the embodiment of the invention thus acquires a multi-functional significance. Without claiming totality, the following functions are listed here: The consolidation of the encapsulating substance on the core material, and simultaneously the fine particulate multi-material mixture of valued- and/or auxiliary substances; the separation of the individual components of the encapsulating substance from each other, and the separation of the complete encapsulating substance from the core material; the release of the enveloping substances, inclusive of the surface of the core material by ready access of cold water; the consolidation particularly of the outer regions of the particles against friction under the conventional conditions of transport, storage, application and the like; the binder can itself be selected as a recipe constituent of the complete mixture; the binder can however also be an additional carrier for loosening- and/or dispersing auxiliaries in order to facilitate gel-free dissolving of the individual components, and the valued material mixture in its totality.

As a consequence, the teaching in the embodiment of the invention facilitates the construction according to type and size, of pre-determinable solid multi-material mixtures, which correspondingly contain in a particle, the totality of the multi-material mixture. They lie here in a pre-determinable form separated from each other, so that an undesirable interaction cannot take place in this phase. Simultaneously, the controlled or controllable release of the multi-component mixture in the aqueous float is possible. Problem parts of this valued- material mixture can be stored in the condition of pre-specified fine dispersion in such a way, and the washing- and cleaning process presented so that undesirable hindrances are eliminated here. The dry solid goods are dust-free, and likewise free of fine particles. A multi-stage textile wash is possible. Finally, the invention creates the possibility of adjusting the visual appearance of the dry particles - for example their degree of whiteness or their colour - in pre-determinable ways. All these controlled adjustable effects are thus derived from the modern presented conception, to make available highly compacted valued- material preparations, for example in the range of 500 to 1300 g/l, particularly 600 to 1200 g/l, which can be adapted in their selection and composition of valued- and auxiliary materials, to the corresponding conditions of washing- and cleaning procedures and/or the constantly changing presentation for optimisation of the individually inserted valued materials - for example from the ecological point of view.

In what follows there will first of all be an intensified investigation of the three essential determining elements for handling in the embodiment of the invention: the core material - also termed "carrier particle" -, the encapsulating substance, or the components used as encapsulating substances, and finally the binding agent/binder for the shell-like encapsulation of the carrier particle.

### Core material /carrier particle and its manufacture

This inner core of the corresponding individual particles of the multi-material mixture in the embodiment of the invention, can itself be formed as a single component or made up of several components. Because as a rule a substantial portion - preferably the predominant portion - of the total particles is formed as a carrier particle, its sufficient compacting is a contributory element. Bulk densities of at least 450 g/l and particularly at least 500 to 600 g/l are preferred for the core material. Precisely the possibility of also forming this carrier particle as a single component, for example from water soluble inorganic and/or organic salts such as soda, alkali silicate, alkali salts of polycarboxylic acids, such as trisodium citrate and the like, opens the way here to higher bulk densities in this inner spherical core. Upper limiting values can also lie for example at 1300 to 1500 g/l, or even higher. Nevertheless, one has to ensure the pre-determinable adjustable water solubility of these core materials.

The core material amounts to at least about 15 to 20% by weight, and particularly at least about 35 to 40% by weight of the total mixture. In the most important implementations, the parts by weight of the core material lie at least about 50% by weight of the total mixture, whereby particular significance can be assigned to the range of about 55 to 90% by weight. The percentages by weight here, are as previously indicated, relate to the total multi-material mixture.

The core material is formed as a single component or from several components, and is thus formed at least of a substantial part of water soluble and/or finely dispersed water-insoluble inorganic and/or organic components of conventional washing- and cleaning agents. For example named here are only materials from the range of textile detergents, the corresponding builder and/or co-builder, alkalinity imparting agents, temperature stable bleaching agents on a basis of hydrogen peroxide, such as perborate compounds. Further examples are at least extensively gel-free soluble surfactant compounds, particularly corresponding anionic surfactants and/or non-ionic surfactants, but also a multiplicity of further conventional small components of textile detergents, which without hesitation can be exposed to the stresses of an adequate compacting step, for example by extrusion. Basically, the carrier particles in the sense of the embodiment of the invention, can be constructed from the group of materials which are provided in the already mentioned older German Patent application DE 195 19 139 (H1795) as constituents for the extrusion, and are there mixed with non-extruded granular further constituents of washing- and cleaning agent mixtures. The individual components should thereby be soluble in an aqueous phase and/or finely dispersed insoluble. In what follows, a summary of compositions of suitable components is given, first of all only as an example - thereby however to give examples of the technical knowledge - and a series of suitable components for the construction of the core material / carrier particle are listed:

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Inorganic soluble or finely divided insoluble detergent constituents such as builder main components - for example zeolite - compounds of the type of zeolite A, X and/or P, alkalisation agents such as soda and waterglass, sufficiently stable carrier salts for hydrogen peroxide, for example sodium perborate salts, but also inorganic salts as auxiliary components, for example sodium sulphate. Suitable organic components can be sufficiently soluble anionic surfactants, for example of the type of alkylbenzol sulphonate or also comparably short-chained alkyl sulphate salts. Non-ionic surfactant compounds in limited quantities, the particular fatty alcohol residues with combined oligo-EO-residues, are likewise suitable mixture components for the core material. Compounds of this type are as a rule free-flowing at room temperature, and are accordingly mixed into the solid core material in limited quantities. Soap as a further surfactant compound, is also a suitable constituent for the construction of the core material.

Other organic mixture components of the carrier particle are for example co-builder components, which form the builder system in admixture with the main builder components. Typical examples of this are compounds of the type of trisodium citrate and/or polymeric polycarboxylates, such as sodium salts of polyacrylic acid or polymethacrylic acid, their co-polymers and/or their co-polymers with maleic acid.

Further constituents of the core material can be water soluble and/or solubility imparting organic components such as polyethyleneglycol and/or its derivatives, which themselves contribute multi-functionality in the manufacture of highly compacted preparation forms of the core material, and its re-dissolving in the aqueous float. Also however, small components, whose incorporation under the comparatively sharp conditions of compacting the carrier material is unobjectionable, can be constituents of the core material/carrier particle. Only named here for example are the known brighteners from the range of textile detergents.

In an important implementation of the teaching in the embodiment of the invention, the following modification is provided: Constituents or even all solitary builders of the carrier particle, can be detergent enzymes, or in their current preparation forms, which contain the detergent enzymes in admixture with carrier substances enclosed in encapsulating substances. In adapting to the corresponding conditions of manufacture of the carrier particle, admixture with further components of the carrier material known up to now, can be taken into consideration, in so far that they refer to general technical knowledge. The particular design encountered here brings about the following important advantage, amongst other things: For storage and handling of detergent preparations, it is known that to safely exclude optionally combined valued materials on an enzymatic basis, is an important basic requirement, in or to prevent undesirable reactions by direct contact. The installation of enzymatic valued materials in the inner core of the spherical multi-layer goods intensifies here on the one hand, the corresponding safety aspects, and on the other hand, by the synchronising of the outer envelope which is in admixture with the spheres present - encapsulating substance/binder in the sense of the definition in the embodiment

of the invention - the homogenising of the spherical goods and the preservation of the homogenous mixture condition can be substantially facilitated. On the grounds of the peculiarities of enzymatic preparations known to the Expert, it can anyhow be expedient in the embodiment of the invention, to make provision for such enzyme additions to the carrier material only in a portion of the individual multi-component particles, in order to synchronise each other in the corresponding finished particles, according to their types of physical properties, so that the homogeneous intermixing of the constituents containing enzymes into the particulate goods free of enzymes, can be guaranteed.

The manufacture of the particulate constructed core material/carrier particles can take place in every optional way known here to the Expert. Particularly suitable for the multi-material mixture in the carrier particle, are conventional compacting processes with simultaneous and/or subsequent moulding into individual carrier particles. In this respect, reference can be made to general technical knowledge. Only named here are for example are processes such as wet granulation, molten agglomeration, spray agglomeration, the fluidized bed in particular, roller compacting and/or other compacting processes. For the relevant Literature, reference is made to the Handbook W. Pietsch " **SIZE ENLARGEMENT BY AGGLOMERATION**", John Wiley & Sons, New York/Salle + Sauerlander, Frankfurt a Main, 1991, as well as the relevant Literature cited therein.

Particular significant for the manufacture of compacted multi-component carrier particles in the sense of the teaching in the embodiment of the invention, of valued material processing, is the means of extrusion and processes employed, for example the processing in the pellet press, respectively connected with subsequent size reduction of the extruded strands, for example by means of impact granulation, and if required, rounding-off the granulates which can still be moulded. Nowadays also, introduced technology, also precisely suitable for textile detergent formulation in practice world-wide, is described in detail in the originally cited EP 0 486 592 and relevant publications. Suitable extrudate particles for example, have bulk densities in the range of 600 to 1100 g/l, and in particular, densities in the range of 750 to 1000 g/l. Taking into consideration the teaching in the embodiment of the invention, the composition of high density agglomerates recovered by extrusion or comparable processes, is constructed to be sufficiently gelling-free, and water soluble, and in here, an optimum access to the recovery of the core material is given for the formation of the carrier particles.

### The encapsulating substance and the method of its application

The encapsulating substance can be immediately bound with good adhesion to the carrier particles. It is also however possible to provide one or more separating layers between the carrier particle and encapsulating substance. This latter named case is only of significance, if with regard to the selection and creation of the components of the encapsulating substance, special effects should be initiated by a practical insertion, if a

delay in dissolving of carrier particles is made desirable. Mentioned here as an example is only a multi-stage textile washing, with time-related control of the working stage(s) introduced. Separating layers of the type met with here, can however acquire a quite different practical significance: By a suitable selection of the separating layer material, this dissolving of the carrier particle in the aqueous float can be promoted or accelerated. This can be particularly valid for such carrier materials, which are not free of gel-forming surfactant compounds, and in the manufacture of the carrier material, have formed a dissolving preventing gelled surfactant layer, at least in the outer shell of the carrier particle.

As a rule anyhow, provision is made for the immediate application of the encapsulating substance on the carrier particle. The encapsulating substance, as already given, can be applied as a single layer, or also consist of several layers. Here also as a rule, the application of a single layered encapsulating substance is the preferred implementation, and technically is not claimed.

The encapsulating substance applied on the carrier particle consists on the one hand, in comparison with the carrier particle as a rule, of fine particulate solid valued- and optionally auxiliaries, which are inserted optionally with admixtures of free-flowing valued material and/or auxiliaries, as well as those which are agglomeration auxiliaries, and a binder which is soluble in cold water and solid at room temperature. These latter components are described individually in a separate treatment which follows, so that first of all here, only the value- and optional auxiliary of the encapsulating substance will be detailed, which is fastened on the carrier particle shell-like by means of the binder.

One or more of the following representatives can be present particularly as solid components of the encapsulating substance: Ground to dust/ or fine particulate, or parts of the core material reduced in size to fine particles; slowly soluble and/or gelled components in the form of selected I-materials and/or in the form of pre-formed multi-material compounds; conventional constituents, particularly also small constituents of washing- and cleaning agents, as long as they are not exposed to the operational conditions of compacting the core material; optionally also components which are quickly soluble in cold water and the swift conditions of the wash float and/or the goods to be cleaned in an earlier phase of the washing procedure; reactive components for subsequent reaction with further reactive constituents of the multi-material mixture, which have to be stored separately with sufficient security away from the corresponding reactive constituents in the storage of the solid goods. The different groups represented here of the solid components of the encapsulating substance are explained by examples in what follows. Taking general technical knowledge into consideration, continuing teaching emerges from this for the construction of valued material mixtures in the embodiment of the invention.

In an initial implementation, the solid components of the encapsulating substance are formed by the core material or at least by essential portions of the core material valued materials. The encapsulating substance differs from the core material by the size of the solid particles when compared with each other. This design can then become significant for example, if known admixtures of washing- and cleaning agents in the embodiment of the spatial arrangement of the invention, should be converted into spheres or pearls, or similarly moulded shapes. Textile detergent mixtures are nowadays always extensively marketed overwhelmingly in the form of free-flowing powders capable of being dispensed, or partially agglomerated, which embraces a very wide particle spectrum of individual particles. Textile detergent mixtures of this type particularly frequently contain substantial quantities of dust portions, which can lead to undesirable annoyance in practical use. The simultaneous fine particles present - for example under conditions of high atmospheric humidity - lead to an undesirable clumping process of the dried valued material mixture, which for example can prevent the portioning of household detergents in longer use of a detergent package, or make it more difficult. The form on offer provided in the embodiment of the invention, of the particularly spherical shape of the multi-material mixtures with solid and preferably non-sticky outer surfaces, and simultaneous selection of the individual spherical diameters in the millimetre range, excludes handicaps of the types depicted.

In the design spoken about here, for example an agglomerated in a known manner and particularly least part compacted admixture of corresponding washing- and cleaning agents with a wide particle spectrum, can thus be provided with one whose particle sizes have been fractionally separated. The particle sizes suitable as core material are then processed in the sense of the embodiment of the invention, with the dust- and fine particles of the same product. Possible coarser particles which occur, can be reduced in size to dust and fine particles, and then returned in this form to the product. The compacting of the multi-material mixture can thus take place in an optional form with the insertion of types of process which have been previously enumerated for the manufacture of the core material/carrier particle in the embodiment of the invention.

The teaching in the embodiment of the invention provides in the next design, the application of only slowly soluble and/or gelling components and/or multi-material compounds as solid portions of the encapsulating substance. Only named here for example are surfactant valued materials of the type of fatty alcohol sulphates with particularly straight chained FA-residues, for example in the range of  $C_{14-18}$ . The teaching in the embodiment of the invention provides here, with regard to the separated storage of these problematic portions in the encapsulating substance and the possible selection in the embodiment of the invention, and predetermination of the individual particles sizes of these problematic constituents, the sufficiently finely dispersed distribution of these portions in the aqueous float itself, can then be guaranteed if no additional measures of solution intervention or gelling curtailment are encountered. In important implementations however, provision can be made here however, to process these problematic components

with the assistance of solution aids for example - approximately of the type of fatty alcohol-oligoethoxylates - into multi-material compounds, and these fine dispersions are then separated from each other, and to incorporate them separated from further constituents in the encapsulating substance, and stored here. It is obvious that substantial help for dispersing and dissolving such problematic constituents, can be given here by the teaching in the embodiment of the invention.

A next group of possible mixture constituents of the encapsulating substance, are further conventional constituents, particularly also small constituents of washing- and cleaning agents, which should not be exposed to the operational conditions of compacting of the core material. Components of this type frequently occur in the form of the finest solid products. Their incorporation into the encapsulating substance, takes care of possible occurring problems. A special feature in this connection has already been detailed here : corresponding, particularly dust-form or very finely divided constituents of the multi-component valued material mixture, can be added to the free-flowing preparation of the binder, and dissolved therein, or dispersed and/or emulsified, and in this form incorporated into the encapsulating substance.

A further example of possible mixture components of the encapsulating substance is then given, if the washing- and cleaning process is to be carried out in several stages. Such an example is present if the textile washing is carried out in a time-related predetermined initial phase, for example under pH values of the wash float which differ from those of the subsequent main washing. Thus it can be desirable to arrange to carry out the main washing under comparatively stronger alkaline conditions, a pre-wash under weaker alkaline conditions, or indeed in the neutral range or weakly acid range. By suitable selection of the corresponding valued materials for regulating the pH in the encapsulating substance, optionally in combination with a solution retarding of the core material, the wide variation of operational parameters spoken about here becomes possible. Further examples of this stepwise design, lie in a previous conditioning of the wash float and/or the textile goods to be cleaned, by the incorporation of particularly swiftly active binders for water hardness, the release of particularly strong wetting and ventilating surfactant portions in the early phase of the washing process, and the like. Here also the teaching in the embodiment of the invention, opens up the technical particularly simple possibility of translating these variations into reality, taking general technical knowledge into consideration.

Finally, a further example of the separated storage of individual components in the encapsulating substance is given : a spatial separation of selected valued material constituents can then also be important in the solid multi-material mixture, if potential reactive components in the admixture come for addition jointly, but their reaction however should first take place in the aqueous phase. A typical example of this is the insertion of bleach components on the basis of salts containing hydrogen peroxide, such as the type of the corresponding perborate compounds and/or percarbonate compounds on the one hand,

as well as the simultaneous incorporation of so-called bleach activators on the basis of components which form per-acids in the wash float with access to  $H_2O_2$ . The teaching in the embodiment of the invention provides optimised possibilities for the simultaneous incorporation of these reactive compounds, with the exclusion of a premature reaction in the solid goods.

The quantity portion of the encapsulating substance preferably amounts to at least about 5 to 10% by weight and particularly at least about 20 to 25% by weight - the % weight in relation to the total multi-material mixture. If the encapsulating substance throughout can amount to more than half of the total mixture, then in important implementations nevertheless one can proceed on the assumption, that the encapsulating substance should form a maximum of about 50% by weight of the multi-material mixture. In concrete implementations, for example, corresponding quantity ranges of the encapsulating substance of about 20 to 45% by weight, and particularly about 25 to 35% by weight have shown themselves to be very advantageous - the % by weight being defined as previously.

As already given previously, the solid components of the encapsulating substance with average particle sizes - specified as sieve numbers - are inserted, which are smaller than the average particle sizes or individual particle sizes of the core material/carrier particle. In this way it is guaranteed that by coating the core material, the formation of the encapsulating substance in the sense of a shell agglomeration round the carrier core takes place. Suitable average particle sizes (sieve numbers) for the solid components of the encapsulating substance are - in agreement with the particle sizes of the carrier particle coming for insertion - particularly have the following values : preferably < 0.8 mm, preferably < 0.6 mm, and particularly < than 0.5 mm. A limitation of the particle sizes downwards for these solid particles of the encapsulating substance is excluded as a rule. Only the finest dust portions can be constituents of the encapsulating substance and/or incorporated into the encapsulating substance by means of free-flowing binders.

It is particularly also provided in the embodiment of the invention, to absorb valued material portions which are free-flowing at room temperature, in the solid components of the encapsulating substance. Named here as examples are the corresponding liquid non-ionic compounds, but however also auxiliaries of quite a different type. An example here are silicone oils, which are known to be foam inhibitors or constituents of foam inhibitors inserted into textile detergent mixtures. It can thus be preferable in the embodiment of the invention, to obviate a premature spreading of such auxiliaries capable of flowing, by their preparation and incorporation in the form of selected multi-material compounds. In this way it is possible to counteract an undesirable delay in dissolving of the anyhow slowly soluble anionic surfactants and/or those which are soluble with gelling.

The solid and optionally absorbed free-flowing valued- and/or auxiliary substances therein of the encapsulating substance, are combined in the finished preparation form of the spherical granulate in intimate admixture with the binder which is solid at room temperature, and particularly at least encapsulated to the predominant part with each other. Thus this combination of the encapsulating substance particles to each other should preferably be so designed to be sufficiently stable, that a considerable friction of the fine goods under the conditions of transport, storage and application of the particulate goods, is eliminated. On the other hand it may be preferable to limit the quantity of the binder to be applied on the solid particles of the encapsulating substance in such a way, that at least partly in this outer shell, a microporous goods structure remains held, which promotes a swift penetration of the aqueous phase into the encapsulating substance. This preferred design of the encapsulating substance in the specified implementation, is however not imperative.

The application of the finely divided encapsulation substance components on the surface of the carrier particle, and its combination thereon with each other, with the incorporation of the binder substance(s) detailed in what follows, takes place expediently in the form, that the fine particulate components of the encapsulating substance are introduced on the carrier particle through incorporation of a free-flowing binder phase, by granulation or agglomeration, and fixed there. Particularly suitable here is the carrying out of this process step in the sense of a molten agglomeration or melt granulation, whereby it is heated to higher temperatures, and a molten binder is inserted as a free-flowing phase. Individual items in this respect are given in what follows. The application process of the encapsulating substance is anyhow not limited to this molten agglomeration or granulation, and other wet processes are also suitable. The encapsulating substance can be formed for example by the incorporation of a binder phase, in which the aqueous preparations - solutions and/or emulsions - of the binder come to be inserted. As a rule this includes a following drying step for the formation of the encapsulating layer. Individual items in this respect are given in what follows.

### **The binder inserted for the formation of the encapsulating substance**

Already originally defined are two important requirements of the binder: The binder should be a solid component at room temperature, simultaneously however, soluble in cold water. Furthermore valid are :

Specified selected components or also multi-component mixtures can be inserted as a binder, which do justice to the poly-functional and originally described significance of these components. Particularly suitable in this connection are organic components with softening- and or melting points not below 45°C, and preferably at least 60°C, whereby a further preferred lower limit for the softening- and/or melting points of the binder substance lies at least at 75°C.

Particular organic components, and thus again particular film-forming organic components can be particularly suitable, which can arrive for insertion as such, or also in admixture with auxiliaries, such as dispersing agents and/or solution aids. The components inserted as binders can possess their own functions in the scope of conventional washing- and cleaning agent mixtures - for example as a co-builder or as a solution aid- and dispersing auxiliary, but other components are also suitable in the sense of the implementation of the invention, which are not conventional constituents of washing- and/or cleaning agents.

A particularly suitable class of organic and thus preferred film-forming binders, are water soluble and/or water dispersible oligomer- and/or polymer compounds of synthetic, half-synthetic and/or natural origin. The relevant literature has particularly discussed water soluble polymer compounds in recent times, referring to the US-American Patent literature in great detail. Reference is made in this connection to the publication which has been issued in book form, Y.Meltzer "WATER-SOLUBLE POLYMERS" Developments since 1978, NOYES DATA CORPORATION, New Jersey, USA (1981). Reference is made here particularly to the compilation in the Capital Market Survey, in the place cited, pages 5 to 15. The most important material classes of water soluble polymer compounds are compiled here, which fundamentally also in the sense of the embodiment of the invention, can come to be inserted in the application of binder components - taking general technical knowledge into consideration.

Acrylamide polymers, acrylic acid- and/or methacrylic acid polymers and -co-polymers, with components containing further free carboxy groups in particular, such as maleic acid, ethylene oxide polymers or polyethylene glycols and their reaction products, polymer compounds on the basis of hydrocarbon compounds of the type of Guar gum, as well as heteropolysaccharides of the type of Gum Arabic or Gum Tragacanth, galactomannan polymers of the type of Locust Bean Gum, water soluble cellulose derivatives, for example of the type of alkylcelluloses, hydroxyalkylcelluloses, carboxymethylcelluloses, polyethylene imine, polyvinyl alcohol and water-soluble vinyl alcohol-co-polymers, polyvinylpyrrolidone, as well as starch and water soluble starch derivatives. The term of polymer compounds defined here, includes in all cases the corresponding oligomer compounds of comparable low molar weights, as far as these components fulfil the described requirements of a binder and its properties in the scope of the embodiment of the invention. Reference in this respect can also be made to general technical knowledge.

Particularly suitable cold water soluble and at the same time solid binder components at room temperature, can be assigned to the range known as co-builders, (meth)acrylic acid-polymer compounds or copolymer compounds with for example maleic acid. Another particularly preferred sphere for the selection of binders or binder components in the sense of the embodiment of the invention, are poly-EO-components or the corresponding derivatives with reactive, and optionally also oleophile molecule



constituents, as long as the whole structure of the poly- or oligo-EO-derivatives fulfil the previously defined basic requirements for the binder.

Fundamentally suitable as adhesive liquids are melts, emulsions, as well as aqueous solutions of binder substances in particular, and here particularly are the corresponding organic oligomer- or polymer compounds, whereby here, components forming films having good adhesion, have acquired particular significance.

In a further design of the invention it is possible to use solid spherical multi-component mixtures which can have an influence on the solvating mechanism in the embodiment of the invention, by controlling the solubility in cold water of the binder. Thus in principle for example, readily water soluble oligo-EO-derivatives, approximately of the type of fatty alcohol ethoxylates with 30 or 40 EO-units in the molecule, can be inserted - in that thereby their solvating behaviour becomes modified when admixed with stronger hydrophobic components - for example fatty alcohols. With the awareness of Expert technical knowledge, the adjustment of the solubility in cold water and the solid condition at room temperature or only slightly temperatures, can be guaranteed. For all that, the incorporation of the oleophilic mixture components makes it possible to control the solubility in cold water, and thus the total solubility in water, so that here, a further possibility of achieving the targeted influence on the multi-component product in its totality can become a reality.

Binders can acquire particular significance from their molecular structure as regards their suitability for insertion into washing- and cleaning agents, in the sphere of valued- and/or auxiliaries. An optionally remaining trivial tackiness of the dried binder components in the room temperature range, can be used for the entrapment of powder in a simple manner, when applying the well known powdering. This can come into consideration, for binders for example on the basis of oligo- or poly-EO-compounds.

As already previously mentioned, the free-flowing binder, as far as itself is concerned, can also be introduced as a carrier for fine particulate solid and/or dissolved valued- and/or auxiliary goods, together with the carrier in the multi-component spheres. In this connection, reference is made here expressly to a special feature : The preparation of the binder capable of free-flow, can also have the addition of additives, particularly also dissolved and/or dispersed auxiliaries to influence the visual appearance of the finished goods, and in this form incorporated into the encapsulating substance. Examples of these are dyestuffs, pigments, brighteners and the like. This opens up the technical simplicity of translating into reality the imparting of a particularly attractive appearance to the spherical dried multi-component mixtures.

This opens up here also the following modification: Should for example soluble and/or fine particulate insoluble dyestuffs or pigments come to be inserted as a coloured finish of the outer shell of the multi-material spheres, then a corresponding final

application shell of the binder soluble in cold water, can guarantee this finish on the outer surfaces of the spheres. In this way one can manage to guarantee if required, strongly distinctive visual effects with the smallest addition of optically perceptible auxiliaries. For the practical insertion into the detergent mixture, an important modification is present here, compared with up to now conventional detergent preparations, with a wide particle spectrum and fine particle sizes.

In this connection, one goes into details of a further parameter for aesthetic appearance and potential acceptance of the multi-material mixture, provided by the shell construction in the embodiment of the invention, because the addition of solid binders under storage conditions, can be freely varied extensively: It is known that a series of ingredients of commercial washing-and cleaning agents, and particularly conventional detergent mixtures, are subject to undesirable odours. This parameter gains significance out of all proportion during the storage of multi-material mixtures in tightly sealed packages. If the packet is opened for the first time, or after a long period of storage, or repeatedly opened, then undesirable odours out of all proportion can make themselves noticeable, and lead to a substantial disturbance of the aesthetic impression. It is accordingly known and conventional to add fragrances or odourous substances to the final multi-component mixtures, in order to cover possible undesirable odours present. According to the teaching in the embodiment of the invention, the individual encapsulation finally of all constituents of the multi-material mixture with the binder which is solid at room temperature and under conventional storage conditions, can achieve here a least substantial decrease of this problem. Independently of this, the teaching includes the incorporation of fragrances or odourous substances anyhow. From what has been previously said, it is however understandable that a further important advantage is derived from the structure in the embodiment of the invention, of the multi-component mixture, which can acquire accompanying decisive significance for practical acceptance.

In the dry goods constructed according to the invention, the respective quantity of binder to be inserted, is determined among other things, by the mixture ratio of core material and encapsulating substance. However, limited quantities of binder substance are sufficient as a rule, to ensure the shell agglomeration of the encapsulating substance on the carrier particle. Accordingly the content of binder in the dry valued material preparations in the embodiment of the invention, conventionally lies above up to about 15 to 20% by weight, and preferably not more than 10% by weight - the % by weight calculated as solid substance, and related to the sum of core material and encapsulating substance. In particular, important implementations are provided again with clearly less content of binder in the dried goods. The quantities of this substance in general do not exceed here values of 5 to 6% by weight. They can lie for example in the range of about 0.5 to 4% by weight - the % weight being defined as before. It has been shown that by the encapsulation of a pre-formed carrier on the basis of extrudate particles with the encapsulating substance in weight ratios of about 2/3 carrier particle to 1/3 encapsulating substance, it is possible to translate the shell agglomeration into reality, with a binder melt already with quantities

of binder in the range of about 1 to 3% by weight. The corresponding spherical solid products excel by being completely dust free, by having uniform spherical shape with high resistance to friction, and simultaneous excellent rinsing-in ability and solubility in the cold, or only slightly heated wash float. Continuing data in this respect can be found in the following description of the preferred manufacturing process for the spherical transformed multi-component valued- goods in the sense of the teaching in the embodiment of the invention.

**The manufacture of agglomerated or granulated multi-layer preparations in spherical form in the embodiment of the invention**

The technology to be inserted for applying the encapsulating substance on the carrier particle, falls in the sphere of shell agglomeration or shell aggregation. Once again in this connection, reference can be made to the known technical knowledge which has appeared in book form, and cited previously, viz. the publication of W. Pietsch in the place cited, "SIZE ENLARGEMENT BY AGGLOMERATION".

In general, the suitable manufacturing process is characterised in that one agglomerates or granulates the core material in the form of a pre-formed carrier particle, with the fine particulate goods of the encapsulating substance in the presence of a binder in free-flowing preparation form, by encapsulation, and the binder is solidified. As a free-flowing binder phase, aqueous preparations of binder substances are suitable on the one hand, whereby here particularly, solutions and/or emulsions come into consideration, but particularly preferred however, is the insertion of the binder as a free-flowing melt.

In known ways, both the types of process spoken about here can be carried out, by spraying the free-flowing preparation of binder on the goods to be agglomerated or granulated, whereby simultaneously core material and fine particulate solid particles of the encapsulating substance are added to the agglomeration zone, and preferably set in motion sufficiently there. The coating of the carrier particle can thus be carried out in rounding-off equipment, in other mixing equipment, but also in the fluidized bed drier. Thus for example, the core material is sprayed with the tacky flowing phase of the binder in a mixer. The finer particles in comparison with the core material, adhere to the surface of the core material which is moved in a rolling motion, becomes solidified and forms there the desired shell encapsulation. Further suitable apparatus comprises rounding-off equipment (spheronizer), dragee making machines, rotating drums, and the already named fluidized bed apparatus.

If one operates with aqueous preparations of the binder, as a rule a drying stage is included in this encapsulating step. The insertion of melts of the binder or binding mixture can eliminate this additional operating stage.

In a preferred implementation, in order to spray the free-flowing binder preparation, provision is made for the incorporation of a blowing gas and the insertion of multi-component nozzles. Thus in a particular implementation, it can be operated as follows : In addition to the binder melt particularly carried in by the blowing gas, a further hot gas phase - as a rule hot air - is blown into the goods to be agglomerated. The short-term adjustment and optimisation of the micro-climate in the region of the surface of the solids is thus possible, and thereby the optimisation of the application and spread of the binder melt on the surfaces to be brought into adhesive contact with each other.

The temperature control particularly in the solid goods in the scope of a molten agglomeration, is determined extensively by the temperature sensitivity of the valued materials or valued parts to be brought into contact with each other. In general the temperature of the solid goods is a maximum in the range of up to 45 or 60°C, and thus is held not higher than the range of melting temperatures of the binder. Taking into consideration the high sensitivity at least of selected constituents of the solid goods, it is however provided in preferred implementations of the invention, that solid goods are inserted at approximately room temperature, or held at only slightly elevated temperatures, and by means of adjustment of the micro-climate over a blown-in hot gas phase, one can guarantee the application and spread of the binder on the surface of the solids, without thereby having to arrive at a substantial elevation of the temperature of the goods.

In what follows, general data relating to valued materials and valued material mixtures are compiled, which can arrive for insertion in the scope of the teaching in the embodiment of the invention in carrier material and/or in encapsulating substance.

The contents of surfactants inclusive of soaps altogether preferably amount to 15 to 40% by weight, an particularly 18 to 30% by weight.

Coming into consideration as surfactants - particularly also in the carrier particle - are both anionic surfactants and also common anionic and non-ionic surfactants.

Coming into consideration as surfactants of the sulphonate type are preferably C<sub>9</sub> - C<sub>13</sub>-alkylbenzol sulphonates, olefine sulphonates, i.e. mixtures of alkene- and hydroxyalkane sulphonates as well as disulphonates, as one obtains for example from C<sub>12</sub> - C<sub>18</sub> -mono-olefines with terminal - or internal double bonds, by sulphonation with gaseous sulphur trioxide and subsequent alkaline or acid hydrolysis of the sulphonation products. Suitable are also alkane sulphonates which are recovered from C<sub>12</sub> - C<sub>18</sub> -alkanes, for example by sulphochlorination or sulfoxidation with subsequent hydrolysis or neutralisation. Further suitable are also the esters of  $\mu$ -sulpho-fatty acids (ester sulphonates), e.g. the  $\mu$ -sulphonated methyl ester of hydrogenated coconut-, palm kernel-, or tallow fatty acids, as well as their di-salts. Thus also coming into consideration are sulphonated fatty acid glycerine esters. Understood as fatty acid glycerine esters are the

mono-, di- and tri-esters, as well as their mixtures, as are obtained by the manufacture by esterification of a mono-glycerine with 1 to 3 moles fatty acid, or by exchange of ester radicals of triglycerides with 0.3 to 2 moles glycerine. Preferred sulphonated fatty acid glycerine esters are thus the sulphonation products of saturated fatty acids with 6 to 22 carbon atoms, for example of caproic acid, caprylic acid, capric acid, myristic acid, lauric acid, palmitic acid, stearic acid or behenic acid. The sulphonation products represent a complex mixture which contains the mono-, di- and tri-glyceride sulphonates with p-standing and/or internal sulphonic acid grouping. Forming as by-products are sulphonated fatty acid salts, glyceride sulphates, glycerine sulphates, glycerine and soaps. If one starts with the sulphonation of saturated fatty acids or hydrogenated fatty acid glycerine ester mixtures, then the portion of  $\mu$ -sulphonated fatty acid di-salts amounts throughout at about 60% by weight, according to each carrying out of the process.

Preferred as alk(en)yl sulphates are the alkali- and particularly the sodium salts of sulphuric acid half esters of  $C_{12}$  -  $C_{18}$  -fatty alcohols, for example from coconut fatty alcohol, tallow fatty alcohol, lauryl-, myristyl-, cetyl-, or stearyl alcohol or the  $C_{10}$  -  $C_{20}$ -oxo alcohols and those half esters of secondary alcohols of this chain length. Further preferred are alk(en)yl sulphates of the named chain length which are obtained on a synthetic petrochemical basis from manufactured straight chained alkyl residues, which have an analogous degradation behaviour as the adequate compounds on the basis of fatty chemical raw materials. Particularly preferred from washing technology interests are  $C_{16}$  -  $C_{18}$  alk(en)yl sulphates. Thus it can also be of particular advantage and particularly advantageous for machine detergents to insert  $C_{16}$  -  $C_{18}$ - alk(en)yl sulphates in combination with low melting anionic surfactants and particularly with such anionic surfactants which have a low Kraft-point, and which show at relatively low wash temperatures of for example room temperature up to  $40^{\circ}\text{C}$ , a low tendency towards crystallisation. In a preferred implementation of the invention, the agents therefore contain mixtures of short chain and long chain fatty alkyl sulphates, preferably mixtures of  $C_{12}$  -  $C_{14}$  fatty alkyl sulphates or  $C_{12}$  -  $C_{18}$  fatty alkyl sulphates with  $C_{16}$  -  $C_{18}$  -fatty alkyl sulphates, or  $C_{12}$  -  $C_{18}$  fatty alkyl sulphates with  $C_{16}$  -  $C_{18}$  fatty alkyl sulphates. Inserted in a further implementation of the invention however, are not only saturated alkyl sulphates but also unsaturated alkenyl sulphates with an alkenyl chain length of preferably of  $C_{18}$  to  $C_{22}$ . Thus preferred particularly are mixtures of saturated overwhelmingly consisting of  $C_{16}$  sulphonated fatty alcohols, and unsaturated, overwhelmingly consisting of  $C_{18}$  sulphonated fatty alcohols, for example those derived from solid or liquid fatty alcohol mixtures of the type of HD-Ocenol® (Commercial product of the Patentee). Thus preferred are weight ratios of alkyl sulphates to alkenyl sulphates of 10 : 1 to 1 : 2 and particularly about 5 : 1 to 1 : 1.

Also suitable as anionic surfactants are 2.3-alkyl sulphates which are manufactured for example according to the US-Patent specifications 3,234,258 or 5,075,041, and can be obtained as commercial products of the Shell Oil Company under the names DAN®.

Also suitable are the sulphuric acid mono esters which are ethoxylated with 1 to 6 moles ethylene oxide, the straight chain or branched C<sub>7</sub> - C<sub>21</sub>-alcohols such as 2-methyl branched C<sub>9</sub> to C<sub>11</sub>-alcohols with an average 3.5 moles ethylene oxide (EO) or C<sub>12</sub>-C<sub>18</sub>-fatty alcohols with 1 to 4 EO. They are inserted into detergents only in relatively small quantities on the grounds of their high foaming capacity, for example in quantities of 1 to 5% by weight.

Preferred anionic surfactants are also the salts of alkylsulphosuccinic acid, which are also termed as sulphosuccinates or as sulphosuccinic acid esters, and represent the monoester and/or diester of sulphosuccinic acid with alcohols, preferably fatty alcohols and particularly ethoxylated fatty alcohols. Preferred sulphosuccinates contain C<sub>6</sub> to C<sub>18</sub>-fatty alcohol residues or mixtures of these. Particularly preferred sulphosuccinates contain a fatty alcohol residue derived from ethoxylated fatty alcohols, which themselves are considered to represent non-ionic surfactants (for description see below). Thus again particularly preferred are sulphosuccinates whose fatty alcohol residues are derived from ethoxylated fatty alcohols with narrow homologue distribution. Equally it is also possible to insert alk(en)ylsuccinic acid with preferably 8 to 18 carbon atoms in the alk(en)yl chain, or their salts.

Preferred anionic surfactants are however alkylbenzol sulphonates and/or both straight chain and also branched alkyl sulphates.

Coming into consideration as further anionic surfactants particularly are soaps, preferably in quantities of 0.1 to 5% by weight, in relation to the whole agent. Saturated fatty acid soaps are suitable, such as the salts of lauric acid, myristic acid, palmitic acid, stearic acid, hydrogenated erucic acid and behenic acid, as well as particularly soap mixtures derived from natural fatty acids, e.g. coconut-, palm kernel-, or tallow fatty acids.

The anionic surfactants inclusive of soaps, can be present in the form of their sodium-, potassium- or ammonium salts, as well as soluble salts of organic bases such as mono-, di- or triethanolamine. The anionic surfactants are preferably present in the form of their sodium- or potassium salts, particularly in the form of the sodium salts.

Preferably inserted as non-ionic surfactants are alkoxylated, advantageously ethoxylated, particularly primary alcohols with preferably 8 to 18 C-atoms, and an average 1 to 12 moles ethylene oxide (EO) per mole alcohol, in which the alcohol residue can be linear or preferably methyl branched in the 2-position, or linear and methyl branched residues in admixture, as are conventionally present in oxoalcohol residues. Particularly preferred are however alcohol ethoxylates with linear residues of alcohols of native origin with 12 to 18 C-atoms, e.g. from coconut-, palm-, tallow fat- or oleyl alcohol, and an average 2 to 8 EO per mole alcohol. Belonging to preferred ethoxylated alcohols are for

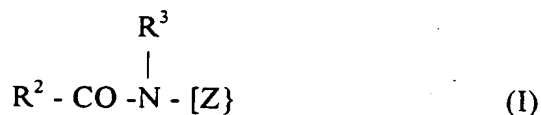
example C<sub>12-14</sub>-alcohols with 3 EO or 4 EO, C<sub>9-11</sub>-alcohols with 7 EO, C<sub>13-15</sub>-alcohols with 3 EO, 5 EO, 7 EO or 8 EO, C<sub>12-13</sub>-alcohols with 3 EO, 5 EO or 7 EO, and mixtures of these, such as mixtures of C<sub>12-14</sub>-alcohols with 3 EO and C<sub>12-18</sub>-alcohols with 5 EO. The given degrees of ethoxylation represented statistical average values, which for special products can be a whole number or a fraction. Preferred alcohol ethoxylates have a narrow homologue distribution (narrow range ethoxylates, NRE). In addition to these non-ionic surfactants, fatty alcohols with more than 12 EO can also be inserted. Examples of these are tallow fatty alcohol with 14 EO, 25 EO, 30 EO or 40 EO.

Apart from these, alkylglycosides of the general formula RO(G)<sub>x</sub> can also be inserted as further non-ionic surfactants, in which R signifies a primary straight-chained or methyl branched or methyl branched aliphatic residue, particularly methyl branched in the 2-position, with 8 to 22, preferably 12 to 18 C-atoms, and G is the symbol that stands for a glucose unit with 5 or 6 C-atoms, preferably for glucose. The degree of oligomerisation x, which gives the distribution of monoglycosides and oligoglycosides, is an optional number between 1 and 10, and x preferably lies at 1.2 to 1.4.

A further class of preferably inserted non-ionic surfactants, which are inserted either as solitary non-ionic surfactants or in combination with other non-ionic surfactants, are alkoxyated, preferably ethoxylated or ethoxylated and propoxylated fatty acid alkyl esters, preferably with 1 to 4 carbon atoms in the alkyl chain, particularly fatty acid methyl esters, as for example are described in the Japanese Patent application JP 58/217598, or preferably manufactured according to the process described in the International Patent application WO-A-90/13533.

Non-ionic surfactants of the type of amine oxide, for example N-coconut-N-N-dimethylamine oxide and N-tallow alkyl-N-N-dihydroxyethylamine oxide, and fatty acid alkanolamides can also be suitable. The quantity of these non-ionic surfactants preferably amounts to not more than that of the ethoxylated fatty alcohols, particularly not more than half of them.

Further suitable surfactants are polyhydroxy fatty acid amides of formula (I),



in which R<sup>2</sup>-CO stands for an aliphatic acyl residue with 6 to 22 carbon atoms, R<sup>3</sup> for hydrogen, an alkyl- or hydroxyalkyl residue with 1 to 4 carbon atoms, and [Z] for a linear or branched polyhydroxyalkyl residue with 3 to 10 carbon atoms and 3 to 10 hydroxyl groups. The polyhydroxy fatty acid amides relate to known materials, which can be obtained conventionally by reductive amination of a reducing sugar with ammonia, an

alkylamine or an alkanolamine, and subsequent acylation with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride. The polyhydroxy fatty acid amides are preferably derived from reducing sugars with 5 or 6 carbon atoms, particularly from glucose.

As already previously demonstrated, the invention includes the implementation in which the composition of the carrier material on the one hand, and the encapsulating substance(s) on the other hand are identical or practical equal, and thus differ only by the particle sizes of the solid particles respectively present in the material portions. In important and preferred implementations anyhow, there are differences throughout in the composition of the valued material or valued material mixture - on the one hand in the carrier particle, and on the other hand in the encapsulating substance. The following example is relevant here:

In a preferred implementation of the invention, the particulate agents contain a carrier particle on an extrudate basis, whereby the portion of the extruded component(s) amount to 50 to 80% by weight, in relation to the whole agent. It is thus further preferred that these extruded components contain surfactants, whereby the content of surfactants in the extruded components amounts to not more than 14% by weight and preferably 6 to 13%, in relation to the extruded components. In a further preferred implementation of the invention, the agents contain extruded carrier components holding surfactants, in quantities such that preparations thereby contain 0.5 to 10% by weight surfactants, in relation to the whole agent.

The extruded components can thus be manufactured by any known process. However it is preferred to use a process according to the teaching of the European Patent EP-B-0 486 592 or the teaching of the International Patent application WO-A-94/09111. The size of the preferred almost spherical carrier extrudate advantageously lies between 0.8 and 2 mm.

The encapsulating substance(s) contain anionic surfactants or anionic, and non-ionic surfactants preferably in quantities of 30 to 95% by weight, in relation to the encapsulating substance. It is particularly preferred that the encapsulating substance contains anionic surfactants, but however is free of non-ionic surfactants. Alkylbenzol sulphonates and/or straight chain and/or branched alkyl sulphates are advantageously inserted as anionic surfactants. The non-extruded granular components and those containing surfactants are thus preferably contained in the agents in quantities so that 2 to 30% by weight, particularly 5 to 25% by weight of surfactants are prepared, respectively in relation to the complete agent.

In a further preferred implementation of the invention, extruded carrier components containing surfactants, and non-extruded encapsulating substances containing surfactants, are introduced, whereby the weight ratio of the extruded components



containing surfactants, to the non-extruded components containing detergents amounts to 6 : 1 to 2 : 1, and particularly 5 : 1 to 3 : 1.

The non-extruded components, particularly for components containing surfactants, can be manufactured by each process known nowadays, for example by means of spray drying, superheated steam drying, spray neutralisation or granulation. Components containing anionic surfactants are particularly preferred, which are obtained in this connection by spray neutralisation according to the older German Patent application P 44 25 968.9, or by granulation and optional simultaneous drying in a fluidized bed according to the teaching of the International applications WO-A-93/04162 and WO-A-94/18303. The particle size distribution of the non-extruded valued materials containing surfactants - also in the form of granulates - should correspond to the previously given requirement : at least in the agent, less than the carrier particle, in order to guarantee its encapsulation. Granulates of almost any optional particle size and particle size distribution, can be manufactured for example in the fluidized bed particularly according to the teaching of WO-A-93/04162. This is also correspondingly valid for the particle size distribution of other granular components, for example an enzyme-granulate, a foam-inhibiting-granulate, a bleach activator-granulate, for their incorporation into the encapsulating substance.

Coming into question as enzymes are those of the class of proteases, lipases, lipolytic active enzymes, amylases, cellulases and their mixtures. Particularly suitable are enzymatic active materials recovered from bacterial sources or fungi, such as bacillus subtilis, bacillus lichenformis and streptomyces griseus and humicola insolens. Preferably inserted are proteases of the subtilisin-type and particularly proteases which are recovered from bacillus lentus. Thus of particular interest are enzyme mixtures, for example those of protease and amylase, or protease and lipase, or lipolytic active enzymes, or protease and cellulase, or from cellulase and lipase, or lipolytic active enzymes, or from protease, amylase and lipase, or lipolytic active enzymes, or protease, lipase or lipolytic active enzymes and cellulase, particularly however, mixtures containing proeases- and/or lipase containing mixtures, or mixtures with lipolytic active enzymes. Examples for lipolytic active enzymes of that type are the known cutinases. Peroxidases or oxidases have also shown themselves to suitable in a few cases. The enzymes are preferably adsorbed on carrier materials and/or embedded in encapsulating substances, in order to protect them against premature decomposition. The portion of enzymes, enzyme mixtures or enzyme granulates can for example amount to about 0.1 to 5% by weight, preferably 0.1 to about 2% by weight.

When inserting into machine washing processes, it may be advantageous to add conventional foam inhibitors. Suitable for example as foam inhibitors, are soaps of natural or synthetic origin, which have a high portion of C<sub>18</sub>- C<sub>24</sub>-fatty acids. Suitable non-surfactant foam inhibitors are for example organopolysiloxanes and their mixtures with microfine, optionally silanised silicic acid, as well as paraffins, waxes, microcrystalline waxes and

their mixtures with silanised silicic acid or bistearylethylene diamide. Also used with advantage are mixtures different foam inhibitors, e.g. those of silicones, paraffins or waxes. The foam inhibitors, particularly silicone- and/or paraffin containing foam inhibitors, are preferably combined on a granular carrier substance which is soluble in water, or can be dispersed in water.

Particularly preferred are thus mixtures of paraffins and bistearylethylene diamide, and mixtures of paraffins and silicones on inorganic carriers. Granulates which contain mixtures of paraffins and silicones in a weight ratio of 1 : 1 to 3 : 1 and under, are particularly preferred in this connection.

In order to achieve an improved bleach activity when washing at temperatures of 60°C and under, bleach activators can be incorporated into the preparations. Examples of these are compounds which under perhydrolysis conditions give rise to aliphatic peroxocarboxylic acids, forming N-acyl or O-acyl compounds, preferably N.N'-tetracylated diamine, p-alkanoyloxy)benzol sulphonate, further carboxylic acid anhydrides and esters of polyols such as glucose penta-acetate. Further known bleach activators are acylated mixtures of sorbitol and mannitol, as are described for example in the European Patent application EP-A-0 525 239. Particularly preferred bleach activators are N.N.N'.N' tetraacetylenediamine (TAED), 1.5-diacetyl-2.4.-dioxohexahydro-1.3.5-triazine (DADHT), and acetylated sorbitol-mannitol mixtures (SORMAN). The content of agents containing bleaching agents of bleach activators, lies in the conventional range. The bleach activators are particularly introduced in the agents in the embodiment of the invention in quantities, so that the agents contain 1 to 10% by weight and preferably 3 to 8% by weight of bleach activator, correspondingly in relation to the whole agents.

Further ingredients of the agents in the embodiment of the invention are preferably inorganic and organic builder substances, bleaching agents, substances which positively influence the washing- out capacity of oils- and fats, greying inhibitors, optionally substances which improve the solubility and speed of dissolving of the individual granular components and/or the whole agent, textile softening materials, optical brighteners, dyestuffs and fragrances, as well as alkaline and/or neutral salts in the form of their sodium- and/or potassium salts.

Suitable as organic builder substances are for example fine crystalline, synthetic, and zeolites containing combined water, in detergent quality. Particularly suitable are zeolite A and/or P, as well as optionally zeolite X and mixtures of A, X and/or P. The zeolite can arrive for insertion as a spray dried powder or also non-dried, stabilised suspension still moist from its manufacture. In the case where the zeolite is inserted as a suspension, it can contain small additions of non-ionic surfactants as stabilisers, for example 1 to 3% by weight in relation to the zeolite, of ethoxylated C<sub>12</sub>-C<sub>18</sub> -fatty alcohols with 2 to 5 ethylene oxide groups, C<sub>12</sub>-C<sub>14</sub>-fatty alcohols with 4 to 5 ethylene oxide groups, or ethoxylated isotridecanols. Suitable zeolites have an average particle size of

less than 10  $\mu$  m (volume distribution: measuring method: Coulter Counter) and preferably contain 18 to 2% by weight, particularly 20 to 22% by weight, combined water. Zeolites can be contained both in the extruded components and also in the non-extruded components.

Suitable substitutes or part substitutes for phosphates and zeolites are crystalline, laminar sodium silicates of the general formula  $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$ , whereby N signifies sodium or hydrogen, x a number from 1.9 to 4, and y is a number from 0 to 20, and preferable values for x are 2, 3 or 4. Crystalline laminar silicates of that type are described for example in the European Patent application EP-A-0 164 514. Preferred crystalline laminar silicates of the given formula are those in which stands for sodium, and x takes the values of 2 or 3. Particularly preferred are both  $\beta$ - and also  $\delta$ - sodium disilicates  $\text{Na}_2\text{SiO}_5 \cdot y\text{H}_2\text{O}$ , whereby  $\beta$ - sodium disilicate can be obtained for example according to the process that is described in the International Patent application WO-A-91/08171. Crystalline laminar sodium silicates can be contained both in the extruded and also in the non-extruded components.

Amorphous silicates, the so-called X-ray amorphous silicates, which do not yield any sharp X-ray reflexes, as are typical for crystalline substances, but at all events have one or more maxima of scattered X-radiation with a breadth of several degree units of diffraction angle, can possess secondary washing capacity, and are also inserted as builder substances. It can even lead to particularly builder properties if the silicate particles in electron diffraction experiments yield washed-out or indeed sharp diffraction maxima. This is to be interpreted in such a way, that the microcrystalline region of the products has a size of 10 to a few hundred nm, whereby values up to a max. 50 nm, and particularly up to 20 nm are preferred. Particularly preferred are thus silicates and silicate-type compounds, for example those according to the older German Patent application P 44 00 024.3, or silicates and silicate compounds, for example obtainable commercially under the terms Nabion 15® and Britesil® (Akzo-PQ). Also particularly preferred are spray dried sodium carbonate -sodium silicate compounds, which in addition can contain surfactants, particularly anionic surfactants such as alkylbenzol sulphonate or alkyl sulphate, inclusive of 2.3-alkyl sulphates. Amorphous silicates and silicate compounds such as the named silicate-carbonate compounds, can likewise be contained in the carrier particle and also in the encapsulating substance.

In addition to the alkali carbonates or instead of them, particularly sodium carbonate, bicarbonates can also be contained in the agents, particularly sodium bicarbonates. Inserted as silicates are above all sodium silicate with a molar ratio of  $\text{Na}_2\text{O} : \text{SiO}_2$  of 1 : 1 to 1 : 4.5, as amorphous silicates with secondary washing capacity, preferably from 1 : 2 to 1 : 3.0. The content in the agents of sodium carbonate and/or sodium bicarbonate thus preferably amounts to up to 20% by weight, advantageously

between 5 and 10% by weight. The content in the agents of sodium silicate generally amounts to up to 30% by weight, and preferably between 2 and 25% by weight.

Useful organic matrix substances are for example polycarboxylic acids, preferably inserted in the form of their sodium salts, such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids, aminocarboxylic acids, nitrilotriacetic acid (NTA), so far as an insertion of that kind is not objectionable on ecological grounds, as well as mixtures of these. Preferred salts are the salts of polycarboxylic acids such as citric acid, adipic acid, succinic acid, glutaric acid, sugar acids and mixtures of these.

Suitable polymeric polycarboxylates are for example the sodium salts of polyacrylic acid or polymethacrylic acid, for example those with a relative molecular mass of 800 to 150,000 (in relation to acid). Suitable co-polymeric polycarboxylates are particularly those of acrylic acid with methacrylic acid, and acrylic acid or methacrylic acid with maleic acid. Co-polymers of acrylic acid with maleic acid have shown themselves to be particularly suitable, which contain 50 to 90% by weight acrylic acid and 50 to 10% by weight maleic acid. Their relative molecular masses, in relation to free acid, in general amount to 5000 to 200,000, preferably 10,000 to 120,000, and particularly 50,000 to 100,000. Also particularly preferred are ter- and quadropolymers, for example those obtained according to DE-A-43 00 772 as monomeric salts of acrylic acid and maleic acid, as well as vinyl alcohol and vinyl alcohol derivatives, or according to DE-C-42 21 381 as monomeric salts of acrylic acid and 2-alkylallyl sulphonic acid, as well as sugar derivatives.

Further suitable builder systems are oxidation products of polyglucosanes containing carboxyl groups and/or their water soluble salts, as are described for example in the International Patent application WO-A-93/08251.

Equally named as further preferred builder substances are also the known polyaspartic acids or their salts and derivatives.

Further suitable builder substances are polyacetals which can be obtained by reacting dialdehydes with polycarboxylic acids which have 5 to 7 C-atoms and at least 3 hydroxyl groups, for example as described in the European Patent application EP-A-0 280 223. Preferred polyacetals are obtained from dialdehydes such as glyoxal, glutaraldehyde, terephthalaldehyde, as well as their mixtures, and from polycarboxylic acids such as gluconic acid and/or glucoheptonic acid.

The organic builder substances can be inserted both in the carrier particle and also in the encapsulating substance, whereby the insertion into the carrier particle can be preferred.

Serving under bleaching agents are compounds which liberate  $H_2O_2$  in water, and sodium perborate tetrahydrate and sodium perborate monohydrate have special significance. Further useful bleaching agents are for example sodium percarbonate, peroxyphosphosphate, citrate perhydrate, as well as peracid salts or peracids liberating  $H_2O_2$  such as perbenzoate, peroxophthalate, diperazelaic acid or diperdodecane diacid. The content of bleaching agents in the agents preferably amounts to 5 to 25% by weight, and particularly 10 to 20% by weight, whereby perborate monohydrate is advantageously inserted. The bleaching agents can be contained both in the carrier particle as well as also in the encapsulating substance of the agents. Thus it is preferred to introduce perborate over the carrier particle in the agents, whilst percarbonate is preferably inserted into the encapsulating substance.

In addition, the agents can also contain components which positively influence the washing out of oils and fats from textiles. This effect becomes particularly clear if a textile is soiled, which has previously been washed several times with a detergent in the embodiment of the invention, which contains these oil- and fat-loosening components, and is then washed. Counted among the preferred oil- and fat loosening components, are for example non-ionic cellulose ethers such as methyl cellulose and methylhydroxypropyl cellulose with a portion of methoxy groups of 15 to 30% by weight, and of hydroxypropoxyl groups of 1 to 15% by weight, respectively in relation to the non-ionic cellulose ether, as well as the polymers of phthalic acid and/or terephthalic acid known from Prior Art, or their derivatives, particularly polymers of ethyleneterephthalates and/or polyethyleneglycol terephthalates, or anionic and/or non-ionic modified derivatives of these. These substances can be contained both in the core and also in the shell, whereby their content in the shell is preferred.

Greying inhibitors have the task of holding in suspension in the float, the soiling loosened from the fibres, and thus preventing the re-deposition of the soiling. Water soluble colloids mainly of an organic nature are suitable in this connection, for example the water soluble salts of polymeric carboxylic acids, glue, gelatine, salts of ethercarboxylic acids or ethersulphonic acids of starch, or cellulose, or salts of acid sulphuric acid esters of cellulose or starch. Water soluble polyamides containing acid groups are also suitable for this purpose. Furthermore, soluble starch preparations and others apart from those starch products named above, can be used, e.g. degraded starch, aldehyde starches etc. Polyvinylpyrrolidone is also useful. Preferred for insertion however, are cellulose ethers such as carboxymethylcellulose (Na-salt), methylcellulose, hydroxyalkyl-cellulose and mixed ethers such as methylhydroxyethyl cellulose, methylhydroxypropyl cellulose, methylcarboxymethyl cellulose and their mixtures, as well as polyvinylpyrrolidone, for example in quantities of 0.1 to 5% by weight, in relations to the agents. These substances can also be contained both in the core and also in the shell, particularly however also in the binder.

The agents can contain constituents in addition, which will raise the speed of dissolving of the individual components and/or the complete agent. Belonging to preferred constituents to be inserted are particularly C<sub>8</sub>-C<sub>18</sub>-alcohols with 10 to 80 moles ethylene oxide per mole alcohol, for example tallow fat alcohol with 30 EO and tallow fat alcohol with 40 EO, but also fatty alcohols with 14 EO, as well as polyethylene glycols with a relative molecular mass between 200 and 2000. Further suitable substances are described for example in the International Patent application WO-A-93/02176.

The agents can contain as optical brighteners, derivatives of diaminostilbene disulphonic acid or their alkali metal salts. Suitable e.g. are salts of 4,4'-bis(2-anilino-4-morpholino-1,3,5-triazinyl-6-amino) stilbene-2,2-disulphonic acid, or similarly constructed compounds, which instead of the morpholino-group carry a diethanolamine group, a methylamino group, an anilino group, or a 2-methoxyethylamino group. Furthermore, brighteners of the type of substituted diphenystyryl can be present, e.g. the alkali salts of 4,4'-bis(2-sulphostyryl)-diphenyl, 4,4'-bis(4-chlor-3-sulphostyryl)-diphenyl, or 4-(4-chlorostyryl)-4'-(2-sulphostyryl)-diphenyl. Mixtures of the previously named brighteners can also be used.

Contained as neutral salts above all are sulphates, and optionally and particularly in detergents are chlorides.

A few fine particulate components can also be used for powdering available granulates, such as for example to decrease the tackiness of the granulates, and to raise the bulk densities of the individual granulates as well as the whole agents. Suitable surface modifiers of that type are known from Prior Art. Suitable in addition to others are thus fine particulate zeolites, silicic acids, amorphous silicates, fatty acids or salts of fatty acids, for example calcium stearate, particularly preferred however, are precipitated silicic acids, mixtures of zeolites and silicic acids or mixtures of zeolites and calcium stearate. Interesting results have arisen - and optionally also even improvements regarding the re-dissolving of agglomerates in aqueous float - by the insertion of antifoam components as optional additions to powdering agents. Fine particulate solid preparations on the basis of silicone oil as components with antifoam activity can be stored in this form in the outer shell of the granulate spheres, and anyhow protected from an undesirable interaction with mixture constituents of the encapsulating substance which hinder solubility.

### Examples

When inserting in the following Table 1, the listed valued material constituents of a textile detergent mixture, they are manufactured according to the data of EP-B-0 486 492 by means of extrusion, impact granulation and subsequent drying of the raw extrudate, whose particle size distribution - determined as sieve numbers - is in % by weight, and compiled in the following Table 3.

The composition of this raw extrudate is as follows :

**Table 1**

Composition of raw extrudate	% by weight
Zeolite A	27.1
Soda	11.4
Na-perborate-monohydrate	17.4
Na-sulphate	5.1
C <sub>9</sub> - C <sub>13</sub> -alkylbenzol sulphonate	9.6
Tallow fat alcohol with 5 EO	0.7
C <sub>12</sub> -C <sub>18</sub> - fatty alcohol with 7 EO	4.3
Co-polymeric sodium salt of acrylic acid	7.1
C <sub>12</sub> -C <sub>18</sub> - fatty alcohol soap	1.2
PEG 400	3.0
Sodium silicate (Na <sub>2</sub> O : SiO <sub>2</sub> 1 : 2.0)	2.1
Brightener	0.4
Water	10.1
Salts	0.5

The granular raw extrudate is united in the following operational step as a carrier material (carrier particle) with the further valued- and auxiliary materials (encapsulating substance) compiled in Table 2, with the insertion of the following identified binder in the sense of a shell agglomeration. Thus given in Table 2 are the quantity ratios of the components inserted for the agglomeration process in % by weight -in relation to the sum of carrier particle and encapsulating substances.

**Table 2**

Composition of the finished product	% by weight
Raw extrudate	66.8
Granulate from 85% by weight of the sodium salt of coconut fatty alcohol sulphate and tallow fat alcohol sulphate in a weight ratio 1:1.2 % by wt.	15.8
Sodium sulphate, the rest non-sulphonated portion and water; manufactured by granulation and simultaneous drying in the fluidized bed	
Tetraacetylene diamine-granulate	8.2
Defoamer-granulate on the basis of a mixture of silicone oil, starch and fatty alcohol	3.64
Soil repellent	2.0
Enzyme mixture	1.56
Powdering agent	1.5
Fragrance	0.42

The following Table 3 combines the particle size distribution - determined according to sieve numbers in % by weight - for the raw extrudate (carrier particle) and the additives (encapsulating substances). Taking into consideration the quantity ratios according to Table 2 for part of the raw extrudate/carrier particle on the one hand, and the mixture components inserted additionally as encapsulating substance, it becomes obvious that the overwhelming part by far of the spherical granulates of carrier particle formed by raw extrudate particles, have a particle diameter > 1.0 mm.

**Table 3:**

Sieve numbers in (%)	Raw extrudate	Anionic surfactant on the basis of FAS	TAED Bleach activator	Defoamer	Soil repellent	Enzyme mixture	Powdering agent
> 1.6 mm	0.1	0	6	0.1	8.8	1.1	1.7
> 1.25 mm	44	0.4	15.6	4	6.9	9.3	2.6
> 1.0 mm	34	13.4	17	9.1	6.8	30.9	2.4
> 0.8 mm	8	19.2	10.8	6.4	4.9	22	2.9
> 0.4 mm	13.5	62	45.6	33.5	31.9	29.3	8.3
> 0.2 mm	0.4% < 0.4 mm	4.7	3.7% < 0.4mm	39.5	28.6	3.5	62.2
> 0.1 mm		0.4		7.3	9	0	16.8
< 0.1 mm		0.2		0.3	2.4	0	2.2

The dissolving behaviour of the corresponding agglomerate spheres are determined by means of the "L-test". For this purpose, the respective agglomerates are investigated by dissolving in water under the following given conditions, and the residues determined gravimetrically. Thus measured are the residues (in % by weight) after a dissolving time of 1.5 minutes under standard conditions, and in a second determination of the residues (in % by weight) after a dissolving time of 5.0 minutes. In individual cases there applied for carrying out this L-test:

Mains water with a water hardness of  $16^0 \text{ dH} \pm 2^0 \text{ dH}$  was used.

The apparatus inserted was defined as follows:

Laboratory stirrer with digital display

Impeller shaft length 350 mm

Propeller stirrer head  $\varnothing$  50 mm

Hand wash test sieve 0.2 mm mesh width

Conventional laboratory equipment.

The carrying out of the test took place individually as follows:

1000 ml tap water was placed in a 2000 ml glass beaker, and the propeller stirrer head inserted centrally about 1.5 cm from the bottom of the glass beaker. The stirrer motor was switched on and adjusted to 800 revs./min  $\pm$  10 revs./min. 8 g of the detergent to be investigated was then added, and stirred for 90 seconds or 5 minutes. The stirrer was removed and cleaned with water. The wash liquor was then poured through the previously weighed sieve, and the glass beaker rinsed out with a little water. The sieve with the



residue was dried to a constant weight in a drying cabinet at  $40^{\circ}\text{C} \pm 5^{\circ}\text{C}$ , and then weighed. A double determination was carried out in each case.

The residual value (% by weight) was calculated as

$$\text{Residue \%} = \frac{\text{weighed out in g} * 100}{\text{original weight in g}}$$

In cases of large differences, a triple determination was carried out. An average value was calculated from the double- or triple determinations.

In addition, the dissolving behaviour was determined by the so-called bowl test. The carrying out of this test was thus undertaken as follows:

25 g of the test agent was added to 5 l tap water ( $30^{\circ}\text{C}$ ) in a water bowl made of dark plastic (for example dark red). After 15 seconds, the agent was distributed by hand in the bowl. After a further 15 seconds, a Turkish towel was immersed in the wash float, and moved about as in a typical hand wash. After 30 seconds, the wall of the bowl was wiped with the towel. After a further 30 seconds wash movement, the towel was extracted and wrung out.

The wash liquor was decanted out of the bowl and the remaining residue after a treatment with 5 to 10 ml was visually observed, and the following signify:

- + unobjectionable, no residue recognisable
- ± scattered but however recognisable, and by critical assessment already disturbing residue
- clearly recognisable and disturbing residue in increasing number and quantity, formation of agglomerates - to clump formation.

The following Examples 1 to 5 give closer data for selection of the binder according to type and quantity of the corresponding agglomeration process inserted, and to the characteristics thus obtained according to evaluation criteria of the L-test and the bowl test, as well as the size distribution of the particles of the agglomerates according to the invention.

The following general data thus applies to the carrying out the respective agglomeration processes:

All the mixture components to be united with each other in the agglomeration stage according to the mixture recipe, were weighed out together, and filled into the selected coating - or agglomeration apparatus.

The binder which is to be inserted, according to the selected recipe is likewise weighed out - either as a melt or aqueous preparation - and filled into the pump receiver. The coating or agglomeration apparatus is started and simultaneously pumping through nozzles begun. The free-flowing binder preparation is sprayed on to the moving contents of the agglomeration apparatus. The spraying procedure was concluded within a few minutes, preferably within 1 to 2 minutes, and in extreme cases after 5 minutes. After the spraying on had ended, there was a short final mixing of about 0.5 to 1 minute, and finally the agglomerate was extracted. Should a melt have been used for spraying through nozzles, then the process has thereby ended. If an aqueous binder preparation was inserted, then this has to include a terminating drying step. For this purpose, the agglomerate is extracted and dried in a fluidized bed drier by means of hot air of about 90°C for a period of time of about 5 minutes, but the temperature of the material should not exceed 65°C thereby (maximum 70°C).

#### Example 1

A mixer was operated as an agglomeration device, in which the solid goods were moved and sprayed with the binder phase. Inserted as a binder liquid phase was a 30% aqueous preparation inserted in the textile detergent as a co-builder, and used under the Trade name "SOKALAN" marketed product (sodium salt of an acrylic acid-co-polymer). This aqueous binder preparation is sprayed on in a quantity of 4% by weight - in relation to the agglomerated solid goods. It was then processed here without an addition of the defoamer component to the agglomeration stage.

#### Example 2

As an amendment of the technology of Example 1, the same valued material mixture in the fluidized bed, was then subjected to an addition of a melt of PEG 4000 as binder for the agglomeration. This binder is solid at room temperature and soluble in cold water, arrives for insertion in a quantity of 2% by weight - in relation to the solid goods to be agglomerated.

#### Example 3

The technical teaching according to Example 1 is repeated. The defoaming components on the basis of a mixture of silicone oil, starch and fatty alcohol is now added subsequently however on to the formed spherical agglomerate, and consolidated there by rolling up.

### Example 4

The teaching of Example 1 is repeated, but here however - deviating from the teaching of Example 1 - the defoaming granulate on silicone basis is added immediately to the multi-component mixture in the mixer, and combined in common with the other components of the encapsulating compound by means of the binder sprayed on.

Determined for the products of Examples 1 to 4 were the corresponding particle spectra, the L-test values after 1.5 min and 5.0 min, as well as the assessment in the bowl test. The respectively determined values or evaluations are compiled in the following Table 4.

**Table 4**

**Mega-pearls 2 for improving the aesthetic appearance**

Particle spectrum (%)	Example 1	Example 2	Example 3	Example 4
> 1.6 mm	51	41	38	52
> 0.8 mm	40	45	48	42
> 0.4 mm	5	13	11	6
> 0.2 mm	2	1	5	0
> 0.1 mm	2	0	0	0
< 0.1 mm	0	0	0	0
Powder properties	Example 1	Example 2	Example 3	Example 4
L-test 1.5 min(% residue)	11	12	10	24
L-test 5.0 min(% residue)	0	0	3	1
Bowl test	+	+	+	+

The numbered values of the particle spectrum of Table 4 show - in comparison to the sieve numbers of Table 3 - the particle distribution and the unification under simultaneous almost complete elimination of fine-and dust portions.

The bowl test is optimised in all extensions of Examples 1 to 4. Also the solubility values are clearly improved or at least sufficient.

### Example 5

A commercial powdered textile detergent mixture, pourable and free-flowing, with a particle size portion > 0.8 mm, of about 50% by weight and a fine particle portion < 0.4 mm, of about 27%, had an addition of a melt of PEG 4000 as binder, and was subjected to the molten agglomeration process in the sense of the teaching in the embodiment of the

invention. By additions following one after the other, the quantity of binder was increased from 1% by weight to 5% by weight.

In all trials, the shell formation agglomeration took place with the formation of spheres, whereby the average spherical diameter likewise increased with the increasing quantity of binder material inserted. Thus finally obtained in this way was a readily soluble agglomerate with at least 80% by weight having a particle size of  $> 0.8$  mm.

#### Patent claims

1. Multi-component pourable and free-flowing washing- and cleaning agents, particularly textile detergents, which combine high density with good solubility also in cold water, and thus facilitates greater freedom in the selection of valued- and optional auxiliary materials, **characterised in that** the following particle structure is formed as abrasion resistant goods free of dust and fine particles, having the following particle structure :
  - a compacted core having good adhesion from one or more valued- and/or auxiliary materials which are soluble in aqueous float, and/or finely dispersed insoluble (core material)
  - encapsulated by a mixture of the same and/or further valued- and/or auxiliary materials with - in relation to the diameter of the core material - smaller individual particle sizes (encapsulating substance)
  - whereby these particles of the encapsulating substance have incorporated a binder material solid at room temperature and soluble in cold water, and are combined on the outer area of the core material (binder).
2. A valued material mixture as Claim 1, characterised in that on access of water, gel-forming and/or only slowly soluble components of the multi-material mixture, are at least the overwhelming portion of constituents of the encapsulating substance whereby this portion has predetermined individual particle sizes.
3. A valued material mixture as Claims 1 and 2, characterised in that its particles have at least a spherical shape, whose size (spherical diameter) preferably lies within the following range : 0.5 to 5 mm, preferably 0.8 to 3 mm, and particularly 1 to 2 mm, whereby it can also be preferred that within a product batch, the spherical goods in its entirety has essentially the same spherical size.
4. A valued material mixture as Claims 1 to 3, characterised in that the core materials constitutes at least of 15 to 25% by weight, preferably at least 35 to 40% by weight, and particularly more than 50% - the % by weight respectively in relation to the whole multi-material mixture - whilst the quantity portion of the encapsulating substance preferably amounts to at least 10% by weight, and particularly less than 20 to 25% by weight (% by weight being defined as before).

5. A valued material mixture as Claims 1 to 4, characterised in that the compacted core material inside the spheres (carrier particle) is formed at least preponderantly of pourable and free-flowing solid material goods by only one carrier particle, which itself can be formed from one- or more components, and particularly in the latter case is manufactured into individual carrier particles by means of a compacting process of a multi-material mixture and simultaneous and/or subsequent moulding.
6. A valued material mixture as Claims 1 to 5, characterised in that the multi-component carrier particle of the core material is manufactured by compacting processes such as wet granulation, molten agglomeration, spray agglomeration in a specially rotating fluidized bed, roller compacting, particularly however by extrusion and compacting process used - as far as it is necessary correspondingly to include moulding into individual carrier particles.
7. A valued material mixture as Claims 1 to 6, characterised in that the carrier material is formed at least to a substantial part by water soluble and/or insoluble inorganic and/or organic components of conventional washing- and cleaning agents which are soluble in water, or finely dispersed in water - for example textile detergent builders and/or co-builders, alkalising agents, temperature stable bleaching agents on a basis of hydrogen peroxide such as perborate compounds-, whereby however - preferred in subordinate quantities - ingredients of organic origin, for example soluble surfactant compounds extensively free of gelling, particularly corresponding anionic surfactants and/or non-ionic surfactants, co-builders, brighteners and the like, which can be constituent(s) of the carrier material.
8. A valued material mixture as Claims 1 to 7, characterised in that washing-and cleaning active enzymes and enzyme preparations are also present as a constituent of the carrier material, whereby preferred here can be that the carrier material containing enzymes is present in only one subordinate parts of the solid spheres.
9. A valued material mixture as Claims 1 to 8, characterised in that the encapsulating substance is immediately combined on the carrier particle with good adhesion, or immediately combined over (a) separating layer(s) with good adhesion to the carrier particle.
10. A valued material mixture as Claims 1 to 9, characterised in that one or more of the following representatives are present as solid material components of the encapsulating substance:
  - dust- and/or fine particulate or parts of the core material reduced in size to fine particulate

- slowly soluble and/or gelled components and/or multi-material compounds
  - conventional constituents, particularly also small constituents of washing- and cleaning agents, as far as they are not subjected to the operating conditions of compacting the core material
  - optionally also components which are quickly soluble in cold water, for swift conditioning of the wash float and/or the goods to be cleaned
  - reactive components for subsequent reaction with further active constituents of the multi- material mixture after they have dissolved in the aqueous float.
11. A valued material mixture as Claims 1 to 10, characterised in that the solid material components of the encapsulating substance with average particle sizes (sieve numbers)  $< 0.8$  mm, preferably  $< 0.6$  mm and particularly  $< 0.5$  mm are applied on the carrier material.
  12. A valued material mixture as Claims 1 to 11, characterised in that parts of the multi-component mixture which are liquid at room temperature, are absorbed in the core material and/or the encapsulating substance, whereby it can be preferred to add non-ionic compounds - particularly from the class of fatty alcohol ethoxylates - at least to a preponderant part of the core material.
  13. A valued material mixture as Claims 1 to 12, characterised in that the encapsulating substance is applied on the carrier particle as a single shell or multi-shell.
  14. A valued material mixture as Claims 1 to 13, characterised in that further additions are made to the encapsulating substance, for example for influencing the visual appearance of the finished goods - for example dyestuffs, pigments, brightener and the like.
  15. A valued material mixture as Claims 1 to 14, characterised in that the binder which is solid at room temperature, for the individual solid components of the encapsulating substance which at least to the preponderant part encapsulates and combines together, and thus this combination of encapsulating substance particles to each other is so designed to be sufficiently stable, so that any friction of the fine goods worth mentioning, is excluded under the conditions of transport, storage and application of the particulate finished goods.
  16. A valued material mixture as Claims 1 to 15, characterised in that the encapsulating substance under insertion of the binder in the scope of a wet agglomeration or - granulation or molten agglomeration or - granulation, is applied on the carrier particle, and is consolidated there.

17. A valued material mixture as Claims 1 to 16, characterised in that the binder is present in quantities of not more than 15 to 20% by weight, preferably not more than 10% by weight, whereby binder contents in the range of 5% by weight, for example 0.5 to 4% by weight can be preferred - the % by weight being correspondingly calculated on solid substance in relation to the sum of the core material and encapsulating substance.
18. A valued material mixture as Claims 1 to 17, characterised in that present as a binder are particularly film-forming organic components with softening - and/or melting points not below 45°C, preferably at least 60°C, and particularly at least 75°C, which can also be mixed with the auxiliaries such as dispersing agents and/or solution aids.
19. A valued material mixture as Claims 1 to 18, characterised in that present as a binder are water soluble and/or water dispersible oligomer- and/or polymer compounds of synthetic, semi-synthetic and/or natural origin.
20. A valued material mixture as Claims 1 to 17, characterised in that a binder or binder mixture are inserted, which at least partly are valued- and/or auxiliary materials from the range of textile detergents.
21. A valued material mixture as Claims 1 to 20, characterised in that the outer shell of the spherical goods - optionally with the incorporation of fine particulate powdering auxiliaries - is developed to be essentially tack-free in the room temperature range.
22. A process for manufacturing washing- and cleaning agents according to Claims 1 to 21, characterised in that one encapsulates the core material in the form of a pre-constructed carrier particle, with the fine particulate goods of the encapsulating substance in the presence of the binder in free-flowing preparation form, and agglomerates or granulates, and consolidates the binder.
23. A process as Claim 22, characterised in that one operates with a particularly aqueous preparation of the binder and subsequent drying, preferably however with a melt of the binder and subsequent cooling of the coated goods.
24. A process as Claims 22 and 23, characterised in that the free-flowing preparation of the binder is sprayed on the goods to be agglomerated or granulated, whereby it is preferred to operate together with a blowing gas.
25. A process as Claims 22 to 24, characterised in that particularly by entry of a binder melt with feeding in an additional hot gas phase into the goods to be agglomerated, it is operated for adjustment and optimising the micro-climate in the region of the

surface of the solid goods, whereby it is preferred that the temperature of this additional gas phase lies above the temperature of the solid goods.

25. A process as Claims 22 to 25, characterised in that for a molten agglomeration, the temperature of the solid goods mixture is held in the range of 45 to 60<sup>0</sup>C and thus higher in the range of the melt temperature of the binder, whereby however it is preferred to operate with temperatures of the solid goods in the melt agglomeration below the melt temperature of the binder.